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INVESTIGATION OF LIQUID ROCKET PROPELLANTS

✷

Contract N7onr-462
Task Order No. III
Project No. NR 220 023

2 January 1953

SECURITY INFORMATION

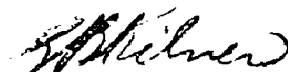INVESTIGATION OF

LIQUID ROCKET PROPELLANTS

Contract N7onr-462

Task Order III

Project NR 220 023

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CONTENTS

CONTENTS (cont.)

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This is the thirty-first in a series of progress reports submitted in partial fulfillment of Contract N7onr-462, Task Order III, covering the work performed during the period from 1 September through 30 November 1952. The previous reports in this series have been issued at bimonthly intervals, this being the first to cover a quarterly period.

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I. INTRODUCTION

A. In February 1948, Contract N7onr-462, Task Order III, was established for the purpose of conducting a comprehensive investigation of liquid propellants suitable for use in rocket motors. Although emphasis has generally been placed on propellant systems possessing high specific impulses, it has often been found desirable to extend the scope of this study to include the short-term investigation of problems arising with any fuel or oxidizer. Pilot plants have been designed and constructed for the manufacture of propellants not commercially available, and these materials have, in turn, been evaluated in a small rocket motor.

B. Results of the investigations have been reported in a series of bimonthly reports, an annual summary being issued at the end of each calendar year. Reports will be issued at quarterly intervals beginning with this report, and no annual summary reports will be prepared henceforth.

C. Of continuing interest to this contract is the development of a high-energy fuel possessing a freezing point below $-65^{\circ}F$ and without excessive vapor pressure at ambient temperatures. Thus, during the period covered by this report, investigations were made on the synthesis of a new compound, N-amino-ethylenimine, and a study of hydrazine additives was continued. Because of the need for an oxidizer capable of being stored in sealed tanks, research is being conducted on improving the physical properties of dinitrogen tetroxide; work has thus far been restricted to determining the effect of several functional groups on the degree of deviation from ideal freezing-point depression. Mono-propellant studies on this contract consist of investigations into the kinetics of decomposition of nitromethane at high pressures. A mass spectrometer and a polarograph are used to determine the extent and manner of decomposition of nitromethane samples placed in a furnace at various initial pressures. Motor testing during this period consisted of a short performance evaluation of "HF-D" hydrocarbon mixture with liquid oxygen, and preliminary work on the determination of the ignition delay of triethyl trithiophosphite with specially prepared WFNA at three different temperatures.

II. KINETIC STUDY OF THE THERMAL DECOMPOSITION OF NITROMETHANE

A. INTRODUCTION

In view of the importance of nitromethane as a monopropellant, an investigation is being made into the mechanism of its thermal decomposition. Several earlier investigations of this problem have been made at subatmospheric pressures; however, this program is being carried out at nitromethane pressures up to 365 psia, in an attempt to simulate more closely the conditions in a rocket combustion chamber. In the earlier work, the progress of the reaction was followed by observation of the variation of total pressure with time. In the present program, it has been possible to determine directly the amount of nitromethane remaining in the partially reacted samples. This procedure allows

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II Kinetic Study of the Thermal Decomposition   Report No. 668
   of Nitromethane, A (cont.)

interpretation of the results to be independent of any postulates concerning the number of moles of product resulting from the decomposition of each mole of nitromethane; thus it allows direct determination of the order of the decomposition with respect to nitromethane concentration. Identification and determination of the relative amounts of products of the decomposition by mass-spectrometer analysis will give more direct evidence for the actual mechanism. During this report period, the main objectives have been to ascertain the order of the reaction with respect to nitromethane at a temperature of 355°C and at pressures up to 365 psia, and to determine the principal intermediate and final decomposition products.

B.   ORDER OF THE REACTION

1.   Frequently, in kinetic studies of complex reactions, the concentration of the reacting compound is determined intermittently or continuously during the course of each experiment. In this way, the rate of the reaction at zero time can be obtained by extrapolation, for each set of initial conditions. In this work, because of difficulties imposed by the high pressures, the alternative was chosen of studying the amount of decomposition in a constant time interval as a function of initial pressure. This technique allows the use of small samples of nitromethane, sealed into glass ampoules, inasmuch as each sample point is the result of a separate experiment.

2.   Weighed amounts of nitromethane were sealed into Pyrex ampoules of 2 to 3 ml volume, immersed in a salt-bath at a controlled temperature for constant times, and quenched rapidly to room temperature. The ampoules were then broken, and the contents analyzed for remaining nitromethane. The initial pressure was calculated from the loading density of the ampoules, assuming that the perfect gas law holds at the temperatures involved. Residual nitromethane was analyzed by means of a polarograph as described in Reference 1. After separation of the nitromethane from the more volatile reaction products, it was diluted quantitatively with 0.05M sulfuric acid and the polarogram of the resulting solution was determined. A representative polarographic wave for nitromethane is shown in Figure 1; the height of the diffusion current wave thus obtained is, in the concentration range used for analysis, proportional to the concentration of nitromethane. Figure 2 is the calibration curve for the analyses, prepared from the analyses of samples containing known amounts of nitromethane.

3.   For constant temperature and reaction time, the integrated rate equations for order 1, 3/2, and 2 with respect to nitromethane reduce to the following:

First order: $\log_e \dfrac{C}{C_o} = K_1$

II Kinetic Study of the Thermal Decomposition
    of Nitromethane, B (cont.)

Report No. 668

Three-halves order:
$$\frac{1}{C^{\frac{1}{2}}} - \frac{1}{C_o^{\frac{1}{2}}} = K_{3/2}$$

Second order:
$$\frac{1}{C} - \frac{1}{C_o} = K_2$$

where

C_o, C = initial and final concentrations of nitromethane

K_1, $K_{3/2}$, K_2 = constants, proportional to the rate constants

Each of these expressions is formally independent of concentration or pressure. By calculating the values of the functions at experimental points over a range of pressures, the approximate order of the reaction can be determined.

4.   A series of thermal decomposition tests was performed at $355^\circ C$ for a period of 31 min and at varying initial pressures. Figure 3 gives the percent decomposition ($100 \times (1 - C/C_o)$) of nitromethane as a function of calculated initial pressure. It is seen, despite the rather large scatter in the data, that there is a definite dependence of percent decomposition upon initial pressure. The dependence cannot be the result of the assumption that the nitromethane behaves as a perfect gas, because the calculated percent decomposition is independent of this assumption. Table I shows the calculated values of the functions defined above, each normalized to a mean of 100 to better show the trends. If the reaction were truly first-order, the values of K_1 of the table (as well as the points of Figure 3) would show no dependence on pressure. Below approximately 300 psia, the apparent order of the reaction is between 1 and 3/2, whereas above 300 psia, indications are that the order is approaching 2. Previous investigators (Reference 2) have found evidence for a first-order law at subatmospheric pressures. Their data, extrapolated to the lower temperature of this work, would indicate approximately 18% decomposition at a pressure of 6 psia, which is not inconsistent with the results shown in Figure 3. Because of this deviation from the first-order decomposition found at low pressures, additional tests will be run to confirm the apparent second-order character of the reaction at high pressures.

      5.   The reaction appears to be mainly homogeneous, as shown by experiments with ampoules to which Pyrex rods had been added. A four-fold increase in the surface-to-volume ratio produced only a 9% increase in decomposition. In another case, a $3\frac{1}{2}$-fold increase in the surface to volume ratio produced a 4% increase in decomposition. The contribution of the Pyrex walls should therefore not be more than 2 to 3%, which is within the experimental error.

C. PRODUCTS OF THE REACTION

      1.   A General Electric mass spectrometer was used in identifying the principal intermediate and final reaction products.

      2.   Two samples were decomposed only partially in order to identify any intermediate reaction products which might also be final products. The only compound identified thus far as a reaction intermediate which does not appear as a final product is nitric oxide. All other compounds appearing in the partly decomposed samples also appear as final products.

      3.   The following materials are the principal final decomposition products of nitromethane under the conditions of high pressure employed in these tests: carbon dioxide, carbon monoxide, water, nitrous oxide, nitrogen, hydrogen cyanide, acetonitrile, and methane. A few other materials are present in trace amounts, but they have not yet been identified. The average concentrations of the principal products are given in Table II. Additional tests are being made to confirm the values.

      4.   A comparison of the partially decomposed and totally decomposed samples, as given in Table II, indicates the following trends:

      a.   The relative amounts of carbon dioxide and acetonitrile remain approximately constant as the decomposition proceeds.

      b.   Nitrous oxide and methane appear as final decomposition products, but do not appear as intermediates. It is possible, however, that their concentration in the partially decomposed samples was below the limits of detection under the experimental conditions employed.

II Kinetic Study of the Thermal Decomposition
    of Nitromethane, C (cont.)

Report No. 568

c.   The concentration of hydrogen cyanide appears to be greater in the partially decomposed samples than in the completely decomposed ones. This may either result from the reaction of hydrogen cyanide with some reaction intermediates, or from its thermal decomposition.

d.   The concentration of nitrogen and carbon monoxide is greater in the totally decomposed samples than in the partially decomposed ones.

5.   Two ampoules containing only acetonitrile were heated in the furnace for a length of time sufficient for the complete decomposition of nitromethane. The mass spectrometric analyses indicated that acetonitrile decomposed less than 5% under the experimental conditions employed, so that, because of the small amount of acetonitrile in the decomposed nitromethane samples, the contribution of decomposition products of acetonitrile may be neglected in the consideration of the nitromethane decomposition.

6.   Table III lists the decomposition products found by Cottrell, Graham, and Reid (Reference 2) for the reaction at 230 to 400 mm initial pressure, and at temperatures ranging from 380 to 410°C. Only materials which were volatile at -78°C were included by the authors. For comparison, the results of the Aerojet work for approximately the same extent of decomposition have been recalculated to exclude water and are also listed in Table III. The differences between the two sets of data are discussed below.

a.   Acetonitrile and hydrogen cyanide have vapor pressures of less than 1 mm at -78°C, so that it is not surprising that Cottrell et al. did not detect these components in the gas phase of their product. Even though they did not find these materials in measurable amounts in the liquid phase, they occasionally detected the faint odor of hydrocyanic acid in their products. The concentrations of hydrogen cyanide and acetonitrile would be expected to be higher in this research. They are probably formed by a bi-molecular process, which would be favored by higher pressures.

b.   Nitric oxide was considered by Cottrell et al. to be the primary nitrogen-containing compound; they find that it decreases from about 60 mole% to 45 mole% as the decomposition reaches about 40%. In this work it was found that nitric oxide comprised about 20 mole% of the decomposition products in the partially decomposed samples and was absent in the completely decomposed ones, so that qualitatively at least the results of the two investigations are similar in this respect. In this laboratory it has been found, however, that more than half of the available nitrogen is in the

form of nitrogen molecules in the partially decomposed samples, and that the
increase in nitrogen gas in the completely decomposed samples corresponds to
the decrease in nitric oxide. In this sense the results are consistent on an
atom-balance basis.

        c.   Cottrell and co-workers found more carbon monoxide
and less carbon dioxide than is found in this work. There is as yet insuf-
ficient information to explain this difference, although again some qualitative
agreement is obtained. In both cases the carbon dioxide concentration remains
virtually constant, and the carbon monoxide concentration increases as the
decomposition proceeds.

        d.   More data are needed to explain the large difference
in the methane concentration in the two investigations.

III. IMPROVEMENT OF DINITROGEN TETROXIDE AS A ROCKET OXIDIZER

A. INTRODUCTION

         Because of its relatively high freezing point ($-11.2^{\circ}C$), dinitro-
gen tetroxide has not received serious consideration as a rocket oxidizer
for Service use. In recent years the so-called "mixed oxides" (dinitrogen
tetroxide and nitric oxide) have become commercially available, and although
this mixture has a freezing point low enough to prevent solidification under
any normal field conditions, the vapor pressure becomes excessive at even
moderately high temperatures. In an attempt to render dinitrogen tetroxide
more valuable for wide-scale rocket application, a search is being conducted/
for additives that will lower its freezing point without increasing the vapor
pressure. By noting the effect of a variety of functional groups on the degree
of deviation from ideality, it is hoped that it will be possible to select
one or more successful additives that will be superior to any selected by
mere random trial of many compounds. Stability and corrosivity of any selected
solutions will be studied before final recommendations are made.

B. APPARATUS

         Apparatus normally used for the measurement of low-temperature
freezing points depends on some relatively gentle oscillatory motion of the
cooling liquid for the establishment of equilibrium. Such stirring tends to
fail exactly when it is most needed, that is, at the first appearance of
solids, and generally after some degree of supercooling. It is difficult to
construct an apparatus incorporating a magnetic stirrer such as is often used
in titrations or reactions requiring an inert atmosphere, because such
stirrers are driven from below, and in the case of a freezing-point apparatus
this area is obstructed by insulating jackets and the cooling bath. As a
torus of Alnico metal of a convenient size, together with apparatus for
magnetizing it were available to this contract, it was possible to construct

III Improvement of Dinitrogen Tetroxide as a   Report No. 668
    Rocket Oxidizer, B (cont.)

the apparatus shown in Figure 4. The stirrer shaft is driven by a cylindrical Alnico magnet, at present unprotected. It is planned to coat this magnet with Teflon, thereby rendering the entire stirrer unit corrosion-resistant to everything except HF. The major advantage of the stirrer is the absence of a rotating seal, which permits its use with air- and water-sensitive systems. Although the stirrer has on occasion been operated at speeds in excess of 1000 rpm, thorough equilibrium is noted at considerably lower speeds. The apparatus was first used to locate the eutectic of the system nitromethane and dinitrogen tetroxide. The higher-temperature portion of the curve was reported in Reference 3. It was found that the freezing temperatures observed with the original equipment were consistent with those obtained by the above-described apparatus at temperatures above $-35^{\circ}C$. Below this point the better equilibrium obtained with the high-speed stirrer shifts the former curve toward somewhat higher temperatures. The complete corrected curve is shown as Figure 5.

    C.   EXPERIMENTAL EVALUATION OF FREEZING POINT ADDITIVES

        1.   Reference 3 presented the freezing-point diagrams for several alkoxy compounds in dinitrogen tetroxide. These compounds are interesting not primarily for direct application as freezing-point depressants for dinitrogen tetroxide, but because of their rather large negative deviation from ideality. It is hoped that by studying a sufficient number of such series, it will be possible to select a compound for actual service use that might not have been obvious beforehand. In addition, the conclusions drawn from this study will perhaps make it possible to synthesize a compound with the desired properties, if one is not immediately available.

        2.   Three additional alkoxy compounds were investigated during this report period. The compounds were diethyl carbonate, $C_2H_5O-\underset{\underset{O}{\|}}{C}-OC_2H_5$;

diethyl oxalate, $C_2H_5O-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-OC_2H_5$; and diethyl Cellosolve, $C_2H_5OCH_2CH_2OC_2H_5$.

Freezing-point diagrams for these compounds with dinitrogen tetroxide are presented as Figures 6, 7, and 8. All exhibit negative deviation, the degree of which is indicated in Table IV.

        3.   Nitromethane in 30 wt% concentration reduces the freezing point of dinitrogen tetroxide to $-35^{\circ}C$, without an adverse affect upon the ignition qualities of the oxidizer with hypergolic fuels (Reference 4). However, a concentration of 48% is necessary to reduce the freezing point to $-55^{\circ}C$. It was hoped that the polynitromethanes would give larger negative deviations from ideality than nitromethane and allow a satisfactory reduction in freezing point with a smaller concentration of additive. However, the

III Improvement of Dinitrogen Tetroxide as a
    Rocket Oxidizer, C (cont.)

Report No. 668

results obtained with the two compounds tested, tetranitromethane and trinitromethane, are disappointing in that both give positive deviations from ideality, and accordingly a very large weight percent of additive would be necessary to depress the freezing point to even minimum requirements. The diagrams for these systems are shown in Figures 9 and 10.

    4. In order not to overlook any possibility of being able to depress the freezing point of dinitrogen tetroxide by the addition of a common oxidizer, the use of concentrated hydrogen peroxide was considered. A specially prepared sample of hydrogen peroxide, analysing higher than 98%, was slowly added dropwise to dinitrogen tetroxide at $0^{o}C$. As each drop touched the surface a vigorous reaction occurred, with the evolution of a considerable quantity of gas. It is not yet known whether the gassing is caused by loss of oxygen from the peroxide due to a high heat of solution, or whether peroxynitric acid (HNO_4), a possible reaction product, is decomposing under these conditions. By distilling dinitrogen tetroxide onto a cooled sample of hydrogen peroxide under vacuum, it should be possible to determine whether or not a stable mixture can be prepared. In the water and dinitrogen tetroxide system, the region of two phases extends from 18 to 87 mole% N_2O_4 at $20^{o}C$; hence, it is possible that, even if a stable solution with hydrogen peroxide can be obtained, limited miscibility might prevent a useful depression of the freezing point.

D.   THERMAL STABILITY OF LOW-FREEZING DINITROGEN TETROXIDE SOLUTIONS

    1. Once an additive has been selected for consideration as a freezing-point depressant for dinitrogen tetroxide on the basis of its degree of lowering and apparent stability, it will be necessary to prove conclusively that the mixture is not only safe to handle, but also that no slow reactions are occurring which might alter the original properties of the solution. The exact method used to determine this stability will depend to a large extent upon the mixture in question. A very simple test can be used, however, for establishing the relative hazard in handling various solutions in the laboratory. This qualitative test involves the sealing of a small quantity of the test solution within a sealed bomb equipped with a rupture disk, and heating the bomb until explosion occurs. The temperature of autodecomposition can then be compared with the known stability of other solutions in the same apparatus.

    2. Selected solutions of some of the additives evaluated as freezing-point depressants were sealed within a small bomb and heated at the rate of $10^{o}F/min$. Results shown in Table V indicate that solutions of trioxane and diethyl Cellosolve in dinitrogen tetroxide should be handled with extreme caution and in limited quantities.
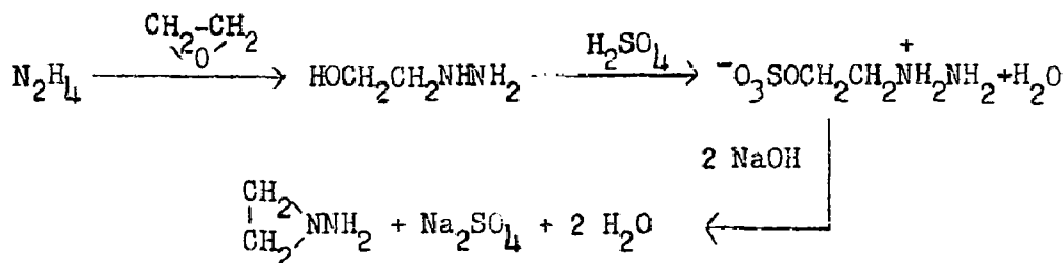
IV. RESEARCH ON THE PREPARATION OF NEW ROCKET PROPELLANTS

A. INTRODUCTION

Inasmuch as it is realized that the mere alteration of existing propellants is not always the solution to producing superior fuels and oxidizers suitable for use in rocket motors, work under this contract includes a program with the purpose of synthesizing new compounds possessing as many desirable properties as possible in one material. At present, interest is centered about the possible synthesis of N-aminoethylenimine because this hydrazine derivative is estimated to have a specific impulse equal to or greater than hydrazine itself (chiefly because of the strain of the three-membered ring) and because early experiments indicated that the compound might have a freezing point considerably lower than hydrazine.

B. METHODS OF PREPARATION OF N-AMINOETHYLENIMINE

1. In analogy to the preparation of ethylenimine, a convenient possible synthesis of N-aminoethylenimine is indicated by the following equations:

$$N_2H_4 \xrightarrow{\overset{CH_2-CH_2}{\diagdown O \diagup}} HOCH_2CH_2NHNH_2 \xrightarrow{H_2SO_4} {}^-O_3SOCH_2CH_2\overset{+}{N}H_2NH_2 + H_2O$$

$$\downarrow 2\ NaOH$$

$$\underset{CH_2}{\overset{CH_2}{\diagup}}\!\!\diagdown NNH_2 + Na_2SO_4 + 2\ H_2O \longleftarrow$$

a. The reaction of hydrazine and ethylene oxide has been previously described (Reference 3); it affords a 51% yield of ethanolhydrazine. Recent observations in experiments with this compound indicate that on prolonged heating (5 to 6 hr) at or near its boiling point slight decomposition occurs, and thus yields are reduced if distillation of a large quantity of the material is attempted.

b. The esterification of ethanolhydrazine was carried out by the method of Leighton (Reference 5). Stoichiometric amounts of ethanolhydrazine and sulfuric acid were separately diluted with one-half their weight of water, and mixed at $0^\circ C$. The resulting colorless solution was heated slowly in an oil bath at 5 mm pressure. The dehydration was interrupted periodically and a portion of the reaction mixture removed. At $60^\circ C$ (temperature of the mixture) the solution was still colorless and solidified to a white crystalline solid on cooling to room temperature. However, subsequent treatment of this solid with aqueous sodium hydroxide failed to yield a product, and it was

consequently considered that the isolated solid was ethanolhydrazinium sulfate, $(HOCH_2CH_2NH_2NH_2)^+$ $(HSO_4)^-$. At $110°$ the solution was decidedly yellow,[*] and set to a glass at room temperature. Partial crystallization occurred after three days at $0°C$, but the process was extremely slow, and isolation of the crystallized from the uncrystallized portion was not accomplished. Further attempts were made to crystallize the material by reducing its viscosity; several solvents (water, ethanol, methanol) were employed, but crystallization did not occur. At $160°C$ the solution was orange, and set to a glass which did not crystallize after two weeks at $0°C$. Further heating resulted in a violent exothermic reaction at about $170°C$. The temperature suddenly rose to $260°C$, and the mass blackened and became cokelike in appearance. That oxidation (probably of the hydrazine function) rather than charring occurred is indicated by the fact that the reaction products were water-soluble, and the odor of sulfur dioxide was easily discernible.

   c. The removal of the elements of sulfuric acid from the ester was attempted by a flash distillation of the ester with hot aqueous sodium hydroxide, according to the directions of Reeves (References 6 and 7). The ester was dissolved in the calculated amount of cold 14% sodium hydroxide, and added dropwise to a well-stirred 14% solution of boiling sodium hydroxide. The distillate was collected at $-5°C$, and the product salted out by addition of solid sodium hydroxide. The $160°$ portion (orange glass) gave about 10% of the expected amount of oil.[**] The $110°$ portion (yellow glass, partially crystalline) gave, on this occasion, about 85%. However, in subsequent experiments it was not found possible to reproduce these results; in six experiments the best yield was only about 10%. The crude oil was alternately dried over sodium hydroxide and fractionally distilled from solid sodium hydroxide. The product obtained had a boiling range of $54-8°C$ at 102 mm.

   d. Variations of this method for the dehydration of ethanolhydrazine were tried in an attempt to increase the yield of product.

   (1) When the ethanolhydrazine and sulfuric acid mixture was heated rapidly over a free flame to $110°$, and the mixture maintained for 30 min at this temperature, only 70% of the reaction water was recovered, but the resulting yellow glass gave a 35% yield of crude product in the subsequent flash distillation. This suggests that the formation of an ether at lower temperatures reduced the yield of desired product in the experiments wherein slow heating was employed:
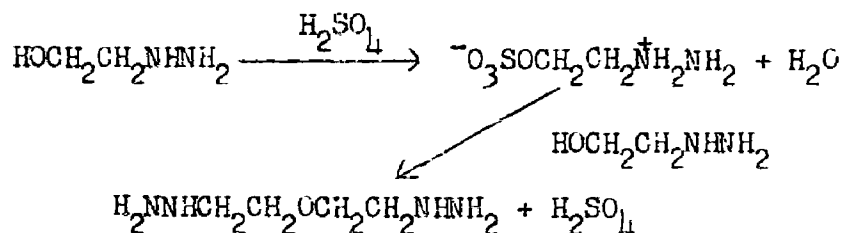
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[*] A dry-ice trap placed between the system and pump had collected 82% of the calculated water of reaction by the time this temperature had been reached.
[**] The yield reported here is based on the weight of crude (wet) product.

$$HOCH_2CH_2NHNH_2 \xrightarrow{H_2SO_4} {}^-O_3SOCH_2CH_2\overset{+}{N}H_2NH_2 + H_2O$$

$$\swarrow \quad HOCH_2CH_2NHNH_2$$

$$H_2NNHCH_2CH_2OCH_2CH_2NHNH_2 + H_2SO_4$$

(2)   Further experiments with the ethanolhydrazine and sulfuric acid mixture, in which the time of reaction, temperature, and mode of addition* were varied produced no increase in the yield of product.

(3)   Variations in the conditions employed in the subsequent flash distillation of the ester produced little or no change in the yield of desired product. The variables considered were the amount and concentration of sodium hydroxide in the boiler, the amount of sodium hydroxide used in salting out the product, and the temperature employed in salting out. If a mixture of the ester and the calculated amount of a 14% sodium hydroxide solution were simply heated without employing a flash distillation, no product was obtained from the aqueous distillate.

2.   In order to avoid undesirable oxidation at high temperatures, phosphoric acid was substituted for sulfuric acid as the esterifying agent (Reference 8). At 160 to 180°C the reaction mixture became dark brown and completely opaque. At 130°C a yellow glass was obtained; a flash distillation of this material afforded no product. A similar experiment with ethanolamine at 160 to 180°C failed to give a crystalline ester. Apparently this reaction represents a true catalytic dehydration without intermediate ester formation. Inasmuch as ethylenimine is known to polymerize readily under acidic conditions, it is presumed that any N-aminoethylenimine formed would polymerize readily in the acidic medium employed.

3.   An attempt was made to prepare N-aminoethylenimine by the dehydrohalogenation of 2-bromoethylhydrazine. The method has been described by Gabriel (References 9 and 10). A chloroform solution of phosphorus tribromide was added dropwise at 0°C to a well-stirred chloroform solution of ethanolhydrazine (Reference 11). A yellow-white precipitate formed during the addition. The mixture was heated at 80°C for one hour to remove volatile materials, and the residue treated with ice water. The solution was filtered to remove a small amount of insoluble material, and the filtrate made basic with sodium hydroxide. The solution was then flash-distilled as described above, but no product could be salted out of the distillate.

---

*An example is the dropwise addition of ethanolhydrazine to hot (135°) sulfuric acid. A stream of nitrogen in this experiment permitted a relatively high reaction temperature without noticeable oxidation.

4. Yields of 50% can now be obtained by a simple modification of the original esterification method. In this new technique, cold undiluted ethanolhydrazine is slowly added to excess concentrated sulfuric acid maintained at 120°C. On cooling and slowly adding small portions of ether, a crystalline product may be obtained. The sulfuric acid solution of the ester is then added to the boiling sodium hydroxide solution, while at the same time additional sodium hydroxide solution is added from another dropping funnel. The product is salted out of the distillate as before.

5. The catalytic dehydration of ethanolhydrazine over activated alumina was considered to be a possible simple and inexpensive method for the production of N-aminoethylenimine. An apparatus was constructed whereby ethanolhydrazine vapors passed through a heated tube containing activated alumina and the products of reaction were collected at -80°C. Reduced pressure promoted rapid passage of the vapor, and a stream of nitrogen was effective both as a carrier and a diluent. The conditions of rapid passage and low concentration of vapor are favorable to the isolation of low-molecular-weight materials, which are thereby removed before further reaction (such as polymerization) can occur. Furnace temperatures ranged from 300 to 500°C, and the reaction times varied according to the rate of nitrogen flow. Experiments of this nature are still in progress, and conclusive results have not yet been obtained. However, in one experiment, in which the furnace temperature was 420°C, a product was obtained having the same boiling range as that from the ethanolhydrazine and sulfuric acid experiments. The following compounds are also possible products in attempting to prepare N-aminoethylenimine by this method: $H_2C = CHNHNH_2$, vinyl hydrazine; $CH_3CH = NNH_2$, acetal hydrazone; and CH_2CH_2NHNH, ethylene hydrazine.

C. PROPERTIES OF N-AMINOETHYLENIMINE

1. The product of the ethanolhydrazine and sulfuric acid experiments is a colorless mobile liquid which tends to polymerize slightly on heating. Its boiling point at atmospheric pressure was found to be about 101°C.[*] A cooling curve displays no break in the region 25 to -150°C. At -80°C the liquid was mobile, by -90°C it had set to a glass, and in the range -130 to -150°C it was a translucent (noncrystalline) solid. The product was titrated with potassium iodate, and consumed 80% of the theoretical amount if a 4-electron change is assumed. A mass spectrogram of the material, in conjunction with spectrograms of pure ethylenimine and unsym-dimethylhydrazine, gave evidence of the presence of the ethylenimine ring, but also indicated the presence of a dimer, probably $(CH_2)_2NHHCH_2CH_2NHNH_2$. Infrared spectra of these same materials lead to inconclusive results, probably because of impurities (such as the dimer) in the desired product. The material tends to discolor (yellow) at room temperature in air - a phenomenon common to alkyl hydrazines and probably due to oxidation.

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[*]Some polymerization occurred at this temperature, and the boiling point is therefore uncertain.

IV Research on the Preparation of New Rocket
   Propellants, B (cont.)

Report No. 668

2.   Work is now in progress to determine the stability of the material, and to characterize it by the preparation of one or more suitable derivatives (as the p-dimethylaminobenzaldehyde hydrazone, for example). The heat of combustion will be determined for evaluation of the compound as a potential rocket fuel.

V.   STUDY OF HYDRAZINE FREEZING POINT DEPRESSANTS

As no completely satisfactory additive, or group of additives, has yet been found for depressing the freezing point of hydrazine without altering desirable qualities of this fuel, the evaluation of new additives is of continuing interest under this contract. Because ethylenimine is now becoming commercially available, is potentially inexpensive, and should possess a specific impulse not much lower than hydrazine, the complete freezing point vs composition diagram was determined for solutions of this material in hydrazine.

1.   The freezing-point diagram is shown as Figure 11. The fact that a solution freezing at -54°C (-65°F) must contain approximately 87 wt% ethylenimine rules out this compound as a practical depressant for hydrazine, although the low freezing point of pure ethylenimine makes it worthy of consideration on its own merits.

2.   The ethylenimine was prepared by the method of Leighton and Reeves (References 5 and 6). It had a boiling range of 55.0 to 55.5°C (750 mm), and a freezing point of -69.0°C. The solution of ethylenimine in hydrazine darkened slightly after standing for two days.

VI.   PERFORMANCE EVALUATION OF THE "HF-D" HYDROCARBON MIXTURE WITH LIQUID OXYGEN

A.   INTRODUCTION

During this report period a complete mixture-ratio survey was made of the propellant combination of "HF-D" hydrocarbon mixture and liquid oxygen. A maximum specific impulse of 227 lb-sec/lb at a mixture ratio of 2.16 was obtained at a nominal chamber pressure of 300 psia in a 100-lb-thrust rocket motor. Although this fuel is of interest primarily because of its hypergolic activity with nitric acid, it was known that another contractor (Reaction Motors, Inc.) was evaluating the material with WFNA; therefore a minimum program was conducted under this contract in order to determine how much greater specific impulse was realizable when liquid oxygen was used as the oxidizer.

VI Performance Evaluation of the "HF-D" Hydrocarbon
  Mixture with Liquid Oxygen (cont.)

B.   TEST INSTALLATION

        The 100-lb-thrust rocket engine previously employed for the
evaluation of propellants on this contract was used for the six tests found
necessary to define the mixture ratio versus specific impulse curve. This
engine is shown in Figure 12, and was described in References 12 and 13.
The injector consisted of ten pairs of one-on-one impinging streams, and a
double-coil turbulator was used approximately 2 in. downstream from the
injector to ensure complete mixing.

C.   PROPERTIES OF THE "HF-D" HYDROCARBON MIXTURE

        The "HF-D" hydrocarbon mixture is a material produced by the
Standard Oil Company of Indiana. Its important physical properties are
shown below:

Carbon, wt%	89.6
Hydrogen, wt%	8.9
Heat of combustion, Btu/lb	16,200
Bromine No.	112.9
Maleic anhydride value	20.8
Freezing Point, $^{\circ}$F	$<-70^{\circ}$

Specific Gravity

+70°F	0.935
+32	0.950
-40	0.990

Viscosity, cs

+70°F	1.4895
+32	2.1923
-40	10.5373

ASTM Distillation, % distilled

	$^{\circ}$F	$^{\circ}$C
IBP	230	110
10	262	128
20	278	137
30	292	144
40	306	152
50	320	160
60	332	167
70	344	173
80	356	180
90	388	198
FBP	424	218

D.   ENGINE TEST RESULTS

1.   Six tests were made over a mixture ratio range of 1.03 to 3.43. A summary of the data, with the performance parameters given both uncorrected and corrected for heat loss to the coolant, is given in Table VI. Plots of specific impulse, characteristic velocity, and thrust coefficient versus mixture ratio are shown in Figure 13.

2.   The runs were characterized by luminous, relatively lengthy, exhaust jets; intermittent streaks indicated the presence of unburnt carbon. Combustion initiation, accomplished by burning gaseous hydrogen and oxygen in the chamber before the introduction of the main propellants, was smooth; but there was always some degree of afterburning on simultaneous termination of fuel and oxidizer flow. The chamber walls, turbulator, and nozzle were covered with carbon on each test.

3.   It is concluded that unless "HF-D" shows exceedingly good hypergolic properties, its use as a rocket fuel is unjustified, as the performance with liquid oxygen compares unfavorably with that of JP-3 or JP-4.

VII.   IGNITION DELAY STUDY OF TRIETHYL TRITHIOPHOSPHITE WITH NITRIC ACID

A.   Contract Amendment No. 7 authorizes a portion of a study with the purpose of correlating ignition delays as measured by various laboratory apparatus with the delays actually observed in rocket motors. Several contractors have been furnished identical samples of triethyl trithiophosphite, n-heptane, and specially purified nitric acid, the composition of which is to be adjusted to 98.5% HNO_3, 1.0% H_2O, and 0.5% NO_2. Ignition delays will be measured at 75, 32, and $-40°F$ for each of the following solutions:

Triethyl trithiophosphite, Vol%	n-Heptane, Vol%
100	0
90	10
80	20
70	30
60	40

B.   As a special report will be issued early in 1953 covering the entire program, no details of the work will be presented at this time. In general, the equipment consists of a small thrust chamber equipped with a photoelectric cell and pressure pickup, both having output signals recorded on an oscillograph. By previously determining the time from activation of the propellant valves to the time of impingement of the fuel and oxidizer streams, it is possible to determine ignition delay, both by rate of increase of chamber pressure and by the occurrence of a steady light-producing reaction.

REFERENCES

1. T. De Vries and R. W. Ivett, Ind. Eng. Chem., Anal. Ed. 13, 339 (1941).

2. T. L. Cottrell, T. E. Graham, T. J. Reid, Trans. Faraday Soc., 47, 584-90 (1941).

3. Aerojet Report No. 820-30, 16 September 1952 (Confidential).

4. Schafert, "Lowering the Freezing Point of U-Stoff," Special Report 1, Halstead Exploiting Centre, Bios/Gp.2./NEC No. 10319, ATI No. 51006.

5. P. A. Leighton, et al., J. Am. Chem. Soc., 69, 1540 (1947).

6. W. A. Reeves, et al., J. Am. Chem. Soc., 73, 3522 (1951).

7. C. F. H. Allen, et al., Org. Syntheses, 30, John Wiley and Sons, New York, N. Y., pp. 38-40 (1950).

8. W. M. Dehn, and K. E. Jackson, J. Am. Chem. Soc., 55, 4435 (1933).

9. S. Gabriel, Ber., 21, 1049 (1888).

10. S. Gabriel, Ber., 28, 2929 (1895).

11. K. Ward, Jr., J. Am. Chem. Soc., 57, 914 (1935).

12. Aerojet Report No. 484, 2 January 1951 (Confidential).

13. Aerojet Report No. 820-27, 24 March 1952 (Confidential).

TABLE I

THERMAL DECOMPOSITION OF NITROMETHANE
ASSUMED RATE CONSTANTS

P_0 psia	percent decomposed	K_1 (1st order)	$K_{3/2}$ (3/2th order)	K_2 (2nd order)
9?	22.0	76	115	167
145	24.6	87	106	123
162	27.8	100	116	129
177	25.8	92	101	107
108	30.7	112	122	128
234	26.1	93	90	83
247	31.2	115	103	98
263	24.4	86	77	67
288	28.8	104	91	77
298	29.1	106	91	75
321	30.0	109	91	73
366	33.0	123	97	74

Temperature, 285°C; time, 31 min
P_0, initial pressure of nitromethane
K_1, $K_{3/2}$, K_2, functions of the percent nitromethane decomposed, proportional to the assumed rate constants

Table I

TABLE II

DECOMPOSITION PRODUCTS OF NITROGLYCERIN

Product	Amount Present, %	
	Partial Decomposition	Complete Decomposition
Acetonitrile	5.2	5.4
Hydrogen Cyanide	2.6	8.0
Carbon Dioxide	22.8	22.4
Nitrous Oxide		3.6
Methane		2.6
Nitric Oxide	13.7	--
Water	9.5	17.3
Carbon Monoxide	7.7	10.6
Nitrogen	30.0	30.0

TABLE III

COMPARISON OF DECOMPOSITION PRODUCTS OF NITROMETHANE (excluding water)

	Amount present, mole%	
Product	Cottrell, et al.	Aerojet Research
Acetonitrile	—	7.4
Hydrogen Cyanide	—	16.6
Carbon Dioxide	7	32
Carbon Monoxide	28	11
Nitric Oxide	46	19.5
Nitrogen	—	13.6
Methane	18	—

Table III

TABLE IV

APPARENT SOLVATION NUMBERS OF ADDITIVES TO DINITROGEN
TETROXIDE AS DETERMINED FROM FREEZING—POINT LOWERING

Additive	Wt%	Mole%	Freezing Point $^{\circ}$C		Apparent Solvation No.
			Observed	Ideal	
Nitromethane	23	30*	−26.5	−24.5	0.3
	51	61*	−59.0	−44.0	0.3
Diethyl Carbonate	35	30*	−39.0	−24.5	1.5
	43	37*	−54.0	−28.0	1.3
Diethyl Oxalate	38	28*	−38.0	−23.5	1.7
Diethyl Cellosolve	35	30*	−29.4	−24.5	0.8
	53	47*	−58.5	−34.0	0.8
Tetranitromethane	46	30*	−23.2	−24.5	(Positive Deviation)
	69	52*	−33.0	−37.5	(Positive Deviation)
Trinitromethane	33	23	−18.2	−21.0	(Positive Deviation)

*Eutectic Mixture

Table IV

TABLE V

THERMAL STABILITY OF DINITROGEN TETROXIDE SOLUTIONS

Additive	Wt% Additive	Vol Sample, ml	Explosion Temp, ^{O}F
$CH_2(OCH_3)_2$ (Methylal)	12.4	1	546
		1	600
		1	548
		1	545
		1	550
	27.7	0.5	No explosion to 577
		0.75	570
		0.75	585
		1	541
		1	556
CH_3NO_2 (Nitromethane)	50.0	1	433
		1	430
$(CH_2O)_3$ (Trioxane)	25.0	1	225
		1	221
Et_2CO_3 (Diethyl carbonate)	25.0	1	552
		1	559
$EtOCH_2CH_2OEt$ (Diethyl Cellosolve)	25.0	1	187
		1	176
		1	140
		1	158

Table V

CONFIDENTIAL

TABLE VI

SUMMARY DATA SHEET

Table VI

CONFIDENTIAL

SERIES NO. D-4-17

TEST NO'S. 1-6

TEST BAY Bldg. 66

PROJECT ENGINEER E. M. Wilson

TEST ENGINEER T. W. Webb

1	2	3	4	5	6	...	10	11	14	15	16	17	18	19	20	22	24	26	27	28	29	30	31	32	PURPOSE	REMARKS
		DATE	DURATION, MAIN PROP. (SEC.)	FUEL	OXIDIZER		CHAMBER PRESSURE	TEST WT. (LBS.)	w_p	MIXTURE RATIO		c^* CALC.	c_e CALC.	I_{sp} CALC.		c_e	I_{sp}	q, Btu/sec	q_c	q_b	q_h	Pilot Light Duration	L^*			
1	1953 10/21	8.0	NH3	O2(liq)	2253/2108		204	67.0	.4492	2.79	1.40	4464	6250	194	1.33	4717	196	130.2	1,440	2,560	0.505	10.5	130	Evaluation of NH3-O2(liq) as propellants	Personnel and instrument checkout. Smooth start, run, shutdown.
2	10/23	11	NH3	O2(liq)	2253/2108		252	79.3	.4211	3.43	1.33	4568	6675	188	1.38	5294	227	130.2	2,300	5,480	0.074	7.0	130	Evaluation of NH3-O2(liq) as propellants	Smooth start, run, shutdown.
3	11/10	12	NH3	O2(liq)	2253/2108		306	96.0	.4670	2.16	1.32	4795	6529	197	1.38	4228	177	169.4	2,260	2,940	1.435	7.0	130	Evaluation of NH3-O2(liq) as propellants	Smooth start, and run. Shutdown rough with afterburning. Excessive carbon deposits on chamber and nozzle.
4	11/13	14	NH3	O2(liq)	2253/2108		199	60.5	.4066	2.00	1.34	4158	5452	169	1.25	4299	159	155.6	1,081	6,674	1.435	8.9	130	Evaluation of NH3-O2(liq) as propellants	Smooth run. Extremely rough start and shutdown with considerable after burning. Excessive carbon deposits on chamber and nozzle.
5	11/14	20	NH3	O2(liq)	2253/2108		128	35.9	.2449	1.03	1.18	4685	6665	153	1.19	4802	207	181.6	6,390	2,580	3.008	6.1	130	Evaluation of NH3-O2(liq) as propellants	
6	11/18	13.6	NH3	O2(liq)	2253/2108		256	83.5	.4170	2.50	1.38			200	1.39							10.0	130	Evaluation of NH3-O2(liq) as propellants	Smooth start, run and shutdown.

All runs with double turbulator.

CONFIDENTIAL

TYPICAL POLAROGRAPHIC
ANALYSIS OF NITROMETHANE
(330 mg in 100 ml of 0.05 M
H_2SO_4)

DIFFUSION CURRENT, μa

VOLTAGE, volts

Figure 1

POLAROGRAPHIC CALIBRATION CURVE
FOR NITROMETHANE ANALYSIS

NITROMETHANE, grams per 100 ml of 0.05N H_2SO_4

DIFFUSION CURRENT, μa x 3.77

X 3.77

C-3305   KHM:em   11-26-52
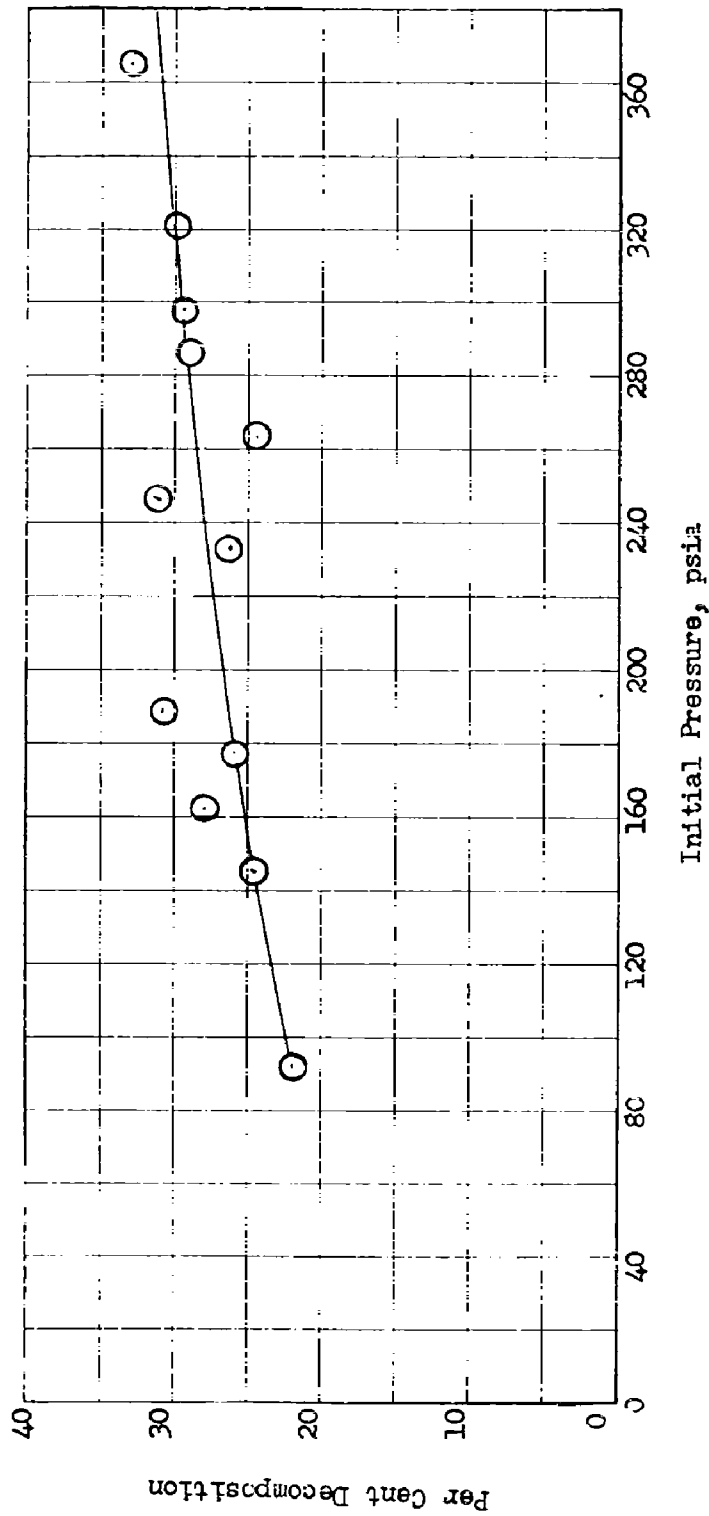
Figure 2

THERMAL DECOMPOSITION OF NITROMETHANE

Temperature = 355 ± 0.05°C
Duration   = 31 minutes

C-3304   KHM:em   11-26-52

Figure 3

FREEZING - POINT APPARATUS

- MOTOR
- CYLINDRICAL MAGNET
- TO VACUUM SYSTEM
- TORUS MAGNET
- RECORDING POTENTIOMETER
- GLASS TUBE FOR AIR INSULATION
- DEWAR
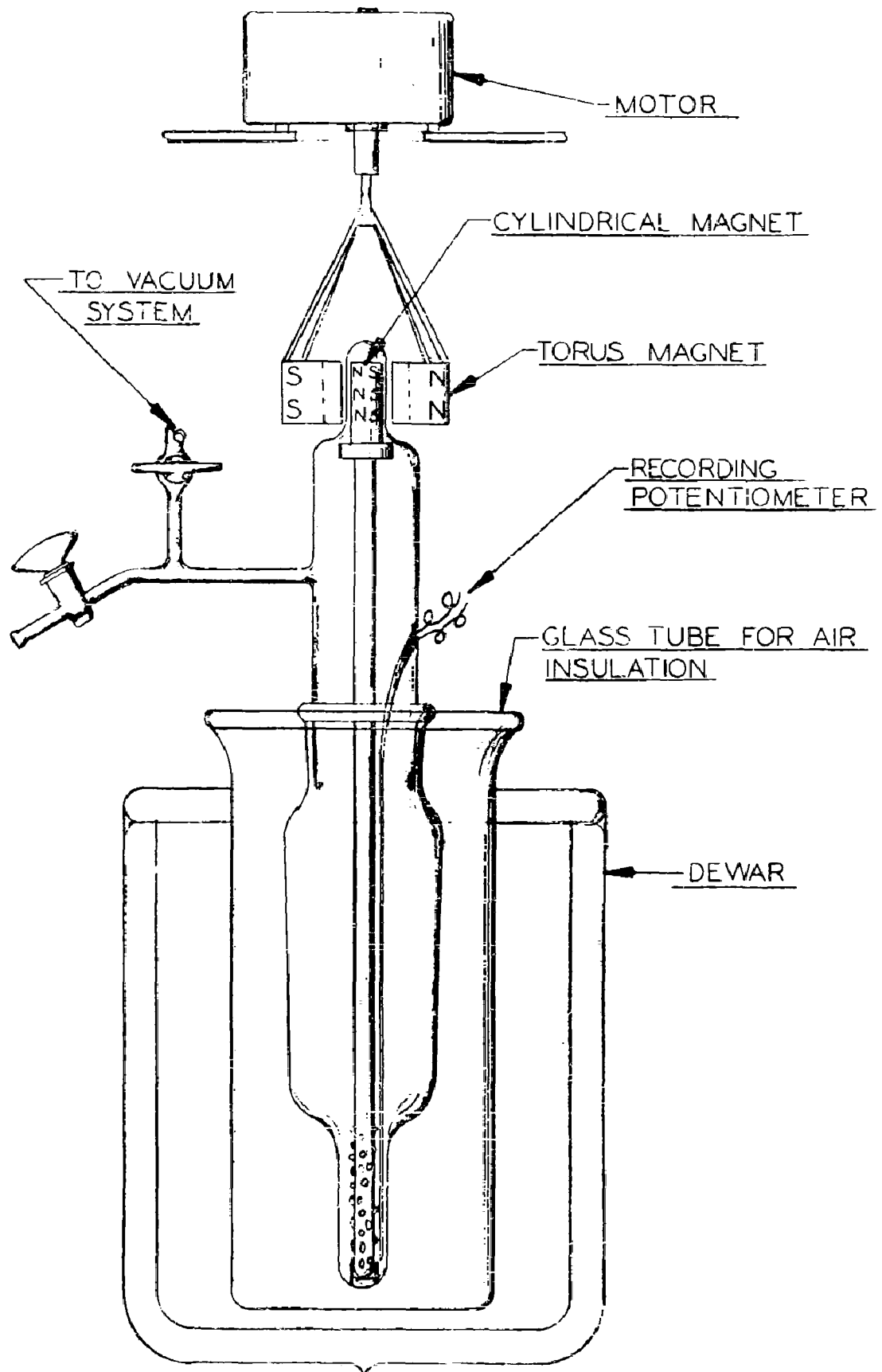
C-3313   12-6-52   EA   E.W.

C-3306   EMW:em   12-4-52

DINITROGEN TETROXIDE—NITROMETHANE
FREEZING-POINT DIAGRAM

WEIGHT PER CENT NITROMETHANE

TEMPERATURE, °C

Figure 5

C-3307   EMW:em   12-3-52

DINITROGEN TETROXIDE—DIETHYL CARBONATE
FREEZING-POINT DIAGRAM

WEIGHT PER CENT DIETHYL CARBONATE

FREEZING POINT, °C
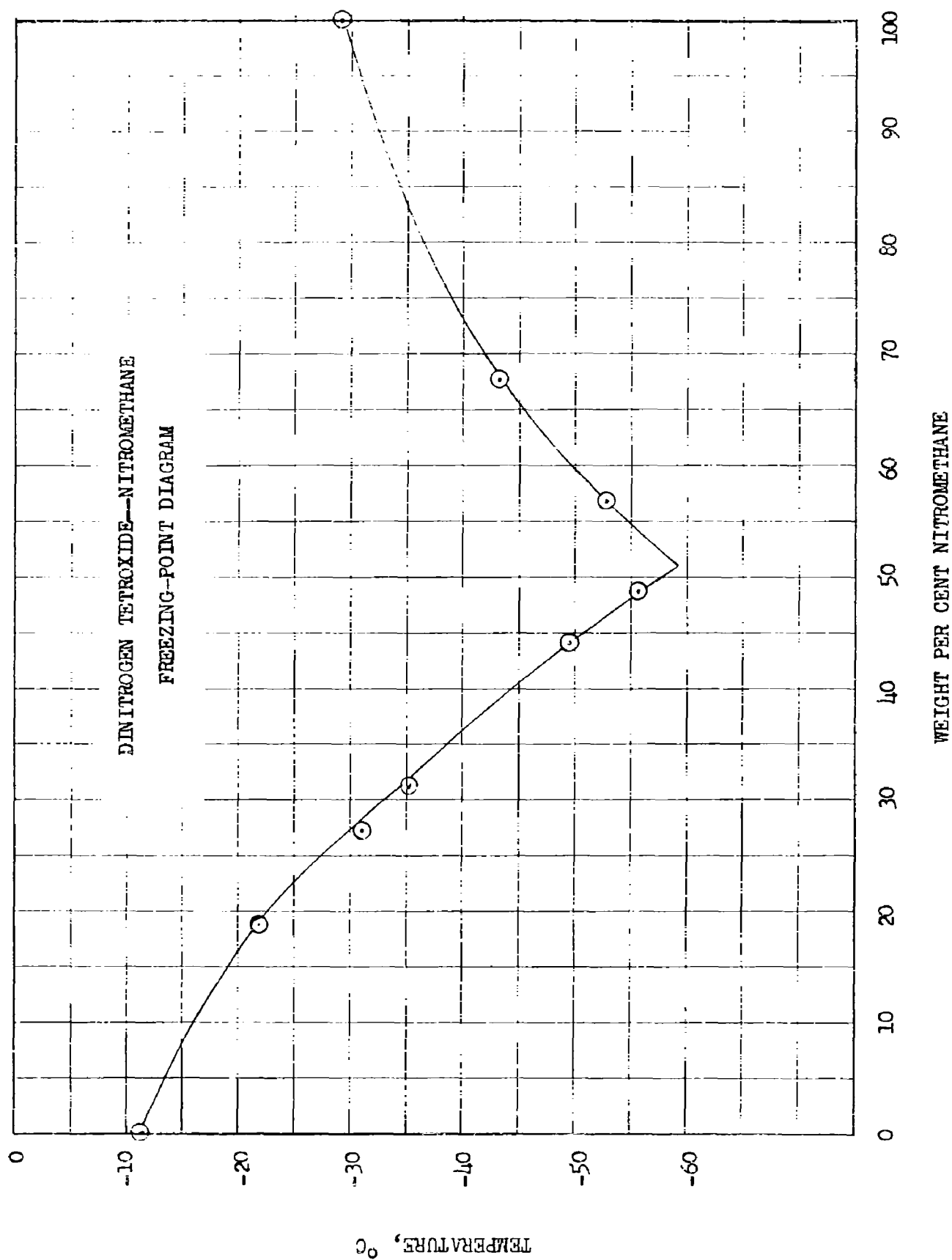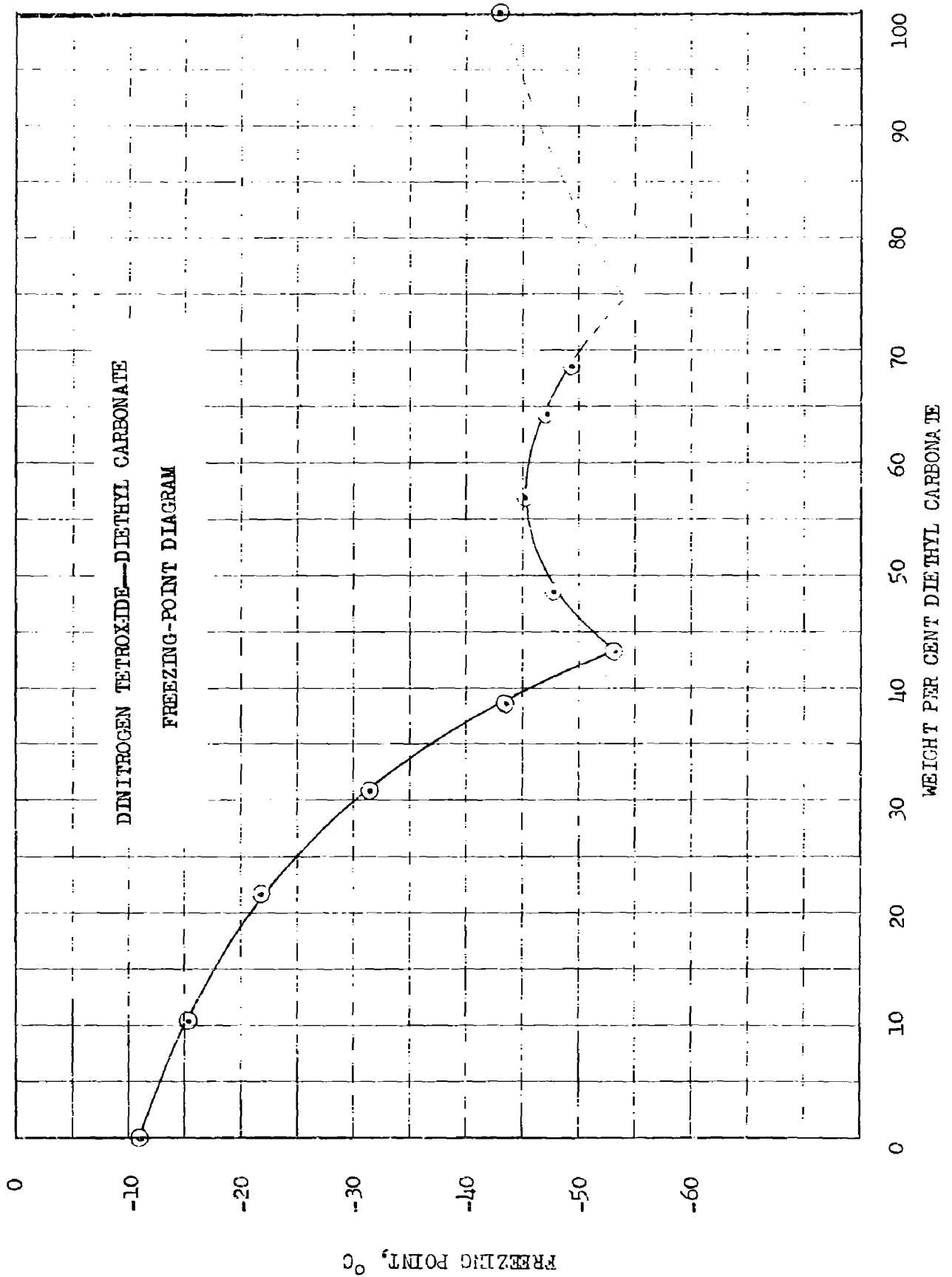
Figure 6

G-3308   EMW:em   12-4-52

DINITROGEN TETROXIDE—DIETHYL OXALATE

FREEZING-POINT DIAGRAM

WEIGHT PER CENT DIETHYL OXALATE

FREEZING POINT, °C

Figure 7
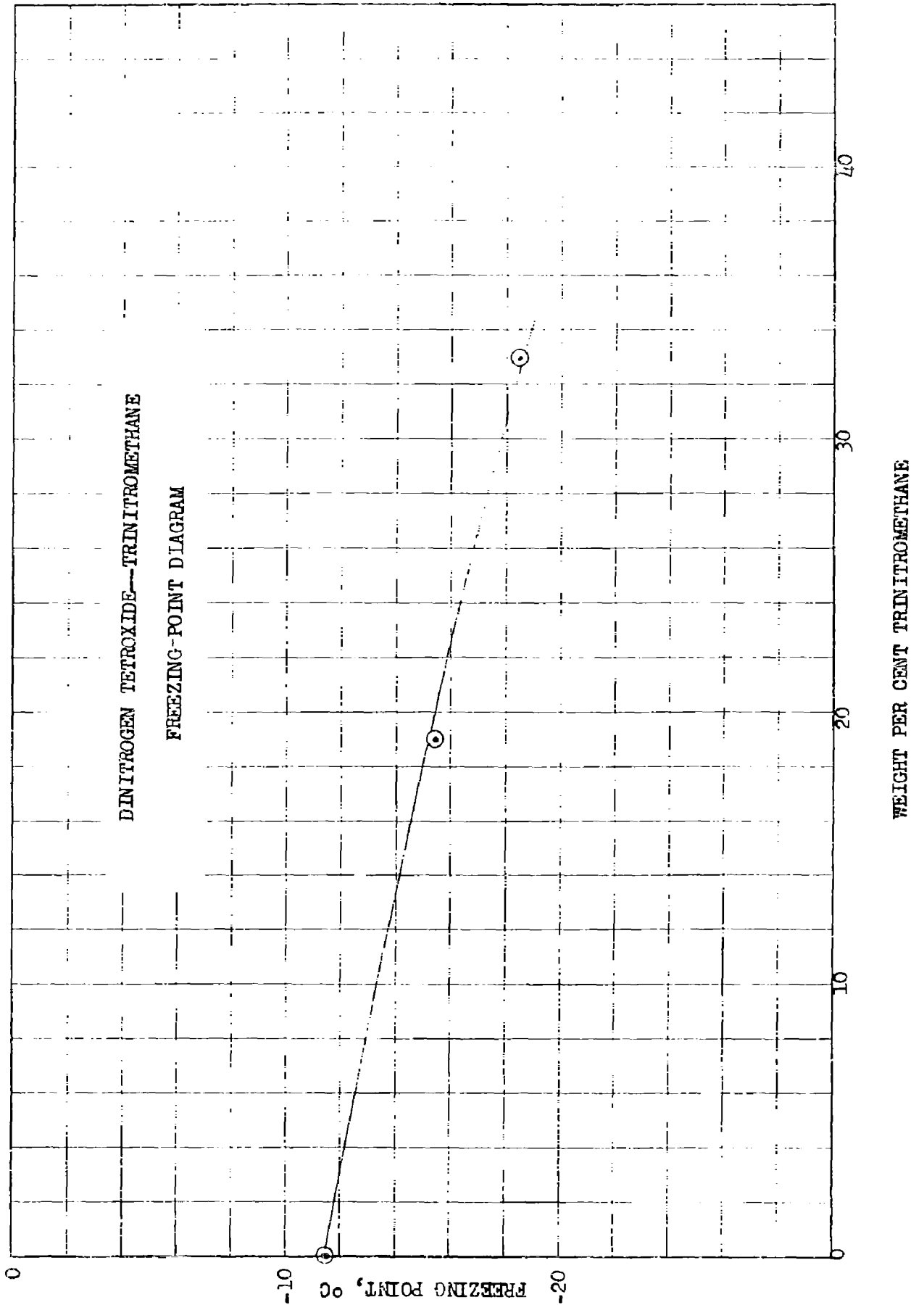
CONFIDENTIAL

Report No. 668

C-3310   EMW:em   12-4-52

DINITROGEN TETROXIDE--DIETHYL CELLOSOLVE
FREEZING-POINT DIAGRAM

WEIGHT PER CENT DIETHYL CELLOSOLVE

FREEZING POINT, °C

Figure 8

C-3312   EMW:em   12-4-52

DINITROGEN TETROXIDE—TETRANITROMETHANE
FREEZING-POINT DIAGRAM

FREEZING POINT, °C

WEIGHT PER CENT TETRANITROMETHANE

DINITROGEN TETROXIDE—TRINITROMETHANE

FREEZING-POINT DIAGRAM

C-3311   EMW:em   12-4-52

C-3309   EMW:em   12-4-52

HYDRAZINE—ETHYLENIMINE
FREEZING-POINT DIAGRAM

WEIGHT PER CENT ETHYLENIMINE

FREEZING POINT, °C

100-lb-Thrust Propellant Tester

PERFORMANCE VERSUS MIXTURE RATIO
"HF-D" HYDROCARBON - LIQUID OXYGEN
Data Corrected For Heat Transfer

Test Nos. D-44-LF 2-6
Thrust ≅ 100 lb
P_c ≈ 300 psia
L* = 130 in.

SECURITY INFORMATION

Figure 13

UNCLASSIFIED